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(6) Application of Solidification Theory to
Rapid Solidification Processing

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Application of Solidification Theory to Rapid Solidification Processing

1. Technical Report Summary

This semi-annual technical report for ARPA Order 3751 covers the period April 1, 1979 to September 30, 1979. Work is reported on the following areas of rapid solidification processing: (1) Microsegregation and Stability at the Solidification Interface, (2) Glass Formation by Rapid Cooling of Eutectic Systems, (3) Compositional Limits Imposed by Thermodynamics during Rapid Solidification and Relative Stability of Heterogeneous Microstructures.

Task Objective

The objective of this work is to investigate the theory of rapid solidification *was investigated* to determine whether major aspects of rapid solidification processes can be explained by conventional solidification theory and to examine non-equilibrium effects which can arise. In particular, segregation effects, glass-forming tendencies, and rules governing the formation of equilibrium and non-equilibrium phases, including alloy composition limits, reaction sequences and metastable phase formation, will be investigated.

Technical Problem and General Methodology

During the freezing of alloys, a planar solid-liquid interface can become unstable; this leads to a cellular or dendritic interface and causes solute microsegregation. The transition between planar and non-planar growth during the directional solidification of binary alloys is being investigated using morphological stability theory. Conventional constitutional supercooling theory predicts that the stability of planar solidification interfaces will decrease as solidification velocities increase. At large solidification velocities, however, morphological stability considerations predict that planar interface stability will increase with solidification velocity. Calculations are being done for rapid solidification conditions to determine the effect of solidification velocity on interface stability.

Eutectic alloy compositions are frequently found to provide favorable conditions for formation of metallic glasses. The theory of how rapidly one needs to solidify to obtain a glassy structure has usually focussed on the

nucleation of the solid phase as the difficult step in crystallization. In the present work, the focus instead is on the growth process. Diffusional sorting of alloy components is necessary to form a two-phase eutectic composite structure. Theoretical predictions can be made of the limitation this imposes on eutectic spacing and at sufficiently rapid solidification rates this diffusional sorting would no longer be possible, perhaps resulting in amorphous solids being formed. Experimental methods designed to solidify eutectic alloys at known velocities and temperature gradients and to test this theory by providing quantitative correlation of alloy microstructure, such as eutectic spacing or glass formation, with solidification conditions are being developed. Two methods are being pursued: (1) rapid directional solidification at controlled speeds up to 10 cm/s and (2) electron beam surface melting for solidification at higher velocities.

Rapid solidification processes are frequently regarded as leading to non-equilibrium conditions which cannot be predicted by theories restricted to conventional equilibrium thermodynamics. Nevertheless, a careful consideration of thermodynamic phase reactions and limits on metastable phases may adequately describe a number of rapid solidification effects. The thermodynamic theory of multiphase systems is being investigated to determine rules that should control metastable reaction sequences, relative stability of heterogeneous microstructure and compositional limits imposed by thermodynamics during rapid solidification.

Technical Results, Important Findings and Conclusions

Detailed methods and results are described in the main body of the report. Important new results, findings and conclusions include:

(a) The solidification interface stability condition in aluminum which contains copper was calculated for a temperature gradient in the liquid of 200 K/cm both in the region where constitutional supercooling is controlling and in the region of higher interface velocity where absolute stability criteria control the major results. The transition between these regions is calculated to occur at about 1 cm/s. The wave length at the onset of instability was found to decrease in both regions as a function of velocity, decreasing monotonically from 0.05 cm when the solidification velocity is 1 μm/s to 0.3 μm when the velocity is 1 m/s.

(b) Directional solidification of the alloy Pd-6% Cu-17% Si was conducted at a velocity of 0.25 mm/s to determine the microstructure in relatively slowly cooled alloys. The microstructure was found to consist of faceted dendrites of a phase, denoted as γ and appearing to be orthorhombic, embedded in a eutectic of γ plus another phase. These phases have been shown not to correspond to any "known" phases in the Pd-Si binary.

(c) The question of the composition limits on the metastable phases that can be formed during rapid solidification was considered in terms of thermodynamic theory. The upper composition limit in surface melted and regrown silicon has been chosen for initial consideration since needed thermodynamic data appear to be available for these binary systems.

(d) Assessment of the relative stability of multiphase systems shows that the ranking of such structures according to their appropriate free energy establishes limits on what structures can evolve from a starting structure.

Significant Hardware Development

A system for controlled directional solidification at known fast solidification velocities is under development.

Special Comments

NBS personnel from this contract have been active in planning and organizing a Second International Conference on Rapid Solidification Processing to be held in Reston, Virginia, March 23-26, 1980 and in organizing sessions and presentation of material on rapid solidification at the DARPA Materials Research Council meeting held in La Jolla, California, July 1979.

Plans and Implications for Further Research

Since the diffusion boundary layer at a solidification interface is calculated to be only a few atom distances when the solidification velocity is 10 m/s, the theory of interface stability as currently developed probably is not valid at such high velocities. Thus, it is planned to investigate modifications of the theory which are required at high growth velocities.

Work will continue on the determination of the phases present in solidified Pd-Cu-Si ternary alloys. The rapid directional solidification device will be tested to determine the maximum solidification velocity attainable based on criteria of planar isotherms. Rapid quenching experiments will be initiated.

Assessment of rules for determining the relative stability of multiphase alloys systems will be pursued. Information concerning an upper composition limit in surface melted and regrown binary silicon systems will be examined.

2. Report of Technical Progress and Results

(1) Microsegregation and Stability at the Solidification Interface

During the freezing of alloys, a planar solid-liquid interface can become unstable; this leads to a cellular or dendritic interface and causes solute microsegregation. The transition between planar and non-planar growth during the directional solidification of binary alloys is being investigated using morphological stability theory. For constant velocity V solidification in the z-direction, the perturbed solid-liquid interface is of the form

$$z = \delta \exp (\sigma t + i\omega_x x + i\omega_y y),$$

where $\delta \exp (\sigma t)$ is the amplitude and ω_x and ω_y are spatial frequencies of the perturbed interface. If the real part of σ is positive for any perturbation (for any values of ω_x and ω_y), the interface amplitude increases exponentially with time t and the planar interface is unstable. If the real part of σ is negative for all possible perturbations, the interface is stable. The value of σ can be determined by solving the heat flow and diffusion equation with appropriate boundary conditions. The basic result is

$$\sigma = V\{-k_L G_L(\alpha_L - V/\kappa_L) - k_s G_s(\alpha_s + V/\kappa_s) - 2\bar{k}T_M\Gamma\omega^2\bar{\alpha} + 2\bar{k}mG_c\bar{\alpha}(\alpha - V/D)/(\alpha - pV/D)\}$$

$$\{k_s G_s - k_L G_L + 2\bar{k}V\bar{\alpha}/\mu + 2\bar{k}mG_c\bar{\alpha}/(\alpha - pV/D)\}^{-1}$$

with

$$\alpha = (V/2D) + [(V/2D)^2 + \omega^2 + \sigma/D]^{\frac{1}{2}},$$

$$\alpha_L = (V/2\kappa_L) + [(V/2\kappa_L)^2 + \omega^2 + \sigma/\kappa_L]^{\frac{1}{2}}$$

$$\alpha_s = -(V/2\kappa_s) + [(V/2\kappa_s)^2 + \omega^2 + \sigma/\kappa_s]^{\frac{1}{2}}$$

$$\bar{\alpha} = (k_s\alpha_s + k_L\alpha_L)/(2\bar{k}),$$

where κ_L and κ_s are thermal diffusivities of liquid and solid, respectively, k_L and k_s are thermal conductivities of liquid and solid, respectively, D is the liquid diffusion constant (diffusion in the solid is neglected), $\omega = (\omega_x^2 + \omega_y^2)^{\frac{1}{2}}$, $\bar{k} = (k_s + k_L)/2$, G_L and G_s are the unperturbed temperature gradients in the liquid and solid, respectively, G_c is the unperturbed

solute gradient i.e., $G_c = Vc_\infty(k-1)/Dk$, k is the distribution coefficient, c_∞ is the bulk solute concentration, T_M is the melting point of the planar interface in the absence of solute, Γ the ratio of the solid-liquid surface energy, γ, and the latent heat of fusion per unit volume, L_v, m is the slope of the liquidus line on the phase diagram, $p = 1-k$, and μ is the linear interface kinetic coefficient. For $\mu \to \infty$, the above equation for σ is in agreement with previous results[1].

For a given alloy and specified values of the processing conditions we can calculate numerically σ as a function of ω, $\sigma(\omega)$, from the above equation. Alternatively, we set $\sigma = 0$ and calculate the bulk concentration c_∞ as a function of ω, $c_\infty(\omega)$. The minimum value of $c_\infty(\omega)$ gives the stability-instability demarcation.

In carrying out calculations we have made the thermal steady state approximation, i.e., let $\kappa_s \to \infty$ and $\kappa_L \to \infty$ in the above equations; this should have little effect on the results. The stability-instability demarcation for aluminum containing copper for $G_L = 200$ K/cm is indicated by the curve in Fig. 1. For a given velocity V for copper concentrations below the curve the planar solid-liquid interface is stable. The straight line with negative slope in the figure is the constitutional supercooling criterion, $mG_c = G_L$ or $c_\infty = G_L Dk/[V(k-1)m]$, for interface stability. The straight line with positive slope is the Mullins-Sekerka absolute stability criterion[2], $mG_c = kT_M\Gamma(V/D)^2$ or $c_\infty = k^2 T_M\Gamma V/[D(k-1)m]$. For small velocities, the constitutional supercooling criterion is a good approximation to the morphological stability calculations. For large velocities the absolute stability criterion is a good approximation. Mullins and Sekerka have shown that the exact curve will always lie above the absolute stability line. Thus, for solute concentrations below those given by the absolute stability equation, the interface is stable. Whereas the constitutional supercooling criterion depends linearly on the temperature gradient in the liquid, G_L, the absolute stability criterion is independent of G_L (although we require that $k_s G_s + k_L G_L > 0$). In Fig. 2, we show the wavelength, $\lambda = 2\pi/\omega$, at the onset of instability as a function of velocity. The wavelength decreases monotonically from 0.05 cm at $V = 1$ μm/s to 0.3 μm at $V = 1$ m/s. Although we show results for $V = 10$ m/s, the theory is no longer valid at such high velocities since the diffusion boundary layer length, D/V, is only a few atomic distances. We are investigating modifications of the theory which are required at high growth velocities.

(2) Glass Formation by Rapid Cooling of Eutectic Systems

Eutectic systems are multicomponent systems in which liquid remains the equilibrium phase to low temperatures because no solid with the same composition is stable. Because of the stability of the liquid at low temperatures these systems have been prime candidates for glass formers by rapid solidification. The theory and practice of how rapidly one needs to solidify has focussed on the nucleation of the solid phase as the difficult step in crystallization.

We have focussed instead on the growth problem. There are two aspects being explored: 1) the thermodynamic question for each system of the existence of a solid phase with the same composition as the liquid which at some temperature below the eutectic becomes stable relative to the liquid, 2) systems in which such a phase does not exist can only crystallize into mixtures of crystals of differing composition. The diffusional sorting of the components is a relatively well understood slow step which may govern the crystallization rate. These ideas have led to a series of predictions for such systems which are being explored experimentally.

Eutectic Solidification Theory

The diffusional sorting of the components in the liquid phase as well as the creation of new surface area between solid phases leads to well known relationships[3] between interface undercooling ΔT, interface velocity V and eutectic spacing λ; namely,

$$V = \frac{D(T)(\Delta T)^2}{4A_1 A_2} ,$$

$$\lambda^2 V = \frac{D(T)A_2}{A_1} ,$$

and redundantly

$$\lambda = 2A_2/\Delta T .$$

Here $D(T)$ is the interdiffusion coefficient in the liquid which is a function of interface temperature and A_1 and A_2 are constants related to the various relevant surface energies, features of the phase diagram and latent heats of the phases. For the present we have applied the extremum principle and assume infinitely fast interface attachment kinetics. If we assume that $D(T)$ obeys an equation,

$$D = D_o \exp(-Q/RT),$$

the velocity can be shown (see Fig. 3a) to have a maximum V_{max} at some interface temperature T_c given by

$$\frac{T_E - T_c}{T_c^2} = \frac{2R}{Q}$$

where T_E is the equilibrium eutectic temperature. The eutectic spacing λ is also shown as a function of temperature in Fig. 3b. The existence of this maximum is, of course, well known for eutectoids and is at least qualitatively the reason for the knee of a TTT curve for the austenite to pearlite transition in steels, for example.

This analysis has a broader application than just for alloys of eutectic composition. At large undercoolings, it is thermodynamically possible and quite probable that alloys with compositions not of eutectic composition can freeze as a two-phase solid. Figure 4a shows the region in temperature and composition where a two-phase solid can form. It is also interesting to note that for kinetic reasons eutectic solidification may occur with metastable phases. Figure 4b shows a hypothetical phase diagram with a total of five eutectics all being possibilities at various temperatures and compositions. The exact possibilities being the subject of Part 3 of this research program.

The purpose of this research is to determine whether this prediction of a maximum crystallization velocity for a eutectic is related to the ease with which certain alloys form glass. This research will be conducted by the solidification of a model glass former over a wide range of solidification velocities. We will determine, at each velocity, the solid phases participating in the eutectic solidification as well as the eutectic spacing. At some critical velocity it is anticipated that no eutectic solidification is possible and the material will form a glass.

Experiments

Experimental methods designed to solidify eutectic alloys at known velocities and temperature gradients are being developed. This is important not only for the study of glass formation, but also for planned experiments on microsegregation. Two methods are being pursued: 1) Rapid Directional

Solidification using the quenching of thin (<1mm) alloy filled tubes in liquid Ga at controlled speeds up to 10 cm/s and 2) Electron Beam Surface Melting for solidification at higher velocities. Both of these methods should permit quantitative determination of solidification conditions which can be correlated to alloy microstructure (e.g., eutectic spacing or glass formation). Method 1) should permit the most accurate determination of interface velocity. The most important consideration is that during directional quenching, the isotherms be essentially planar and move through the sample at a rate determined by the motion of the sample. In method 2), interface velocities must be calculated based on an analysis[4] of heat flow.

The alloy chosen for this research is Pd-6 a/o Cu-17 a/o Si because of its reported low quench rate required for glass formation. Because of controversy concerning the phase diagram of Pd-Si[5,6] and general absence of literature on the ternary Pd-Cu-Si, directional solidification of the alloy was conducted at a velocity of 0.25 mm/s to determine the phases present and the microstructure on relatively slowly cooled alloys. The microstructure consists of faceted dendrites of a phase we will denote as γ embedded in a eutectic of γ plus another phase we will call κ (see Fig. 5).

Electron and x-ray diffraction have been performed on these samples. These phases have been shown not to correspond to any "known" phases in the Pd-Si binary. The γ-phase appears to be orthorhombic with a = 7.46 A°, b = 9.07 A°, and c = 10.83 A°. Electron microprobe analysis of the compositions of the phases is being performed.

Future Work

Work will continue on the determination of the phases present in solidified Pd-Cu-Si ternary alloys. The rapid directional solidification device will be tested to determine the maximum solidification velocity attainable based on a criterion of planar isotherms. Rapid quenching experiments will be initiated.

(3) Formation of Equilibrium and Nonequilibrium Phases

Compositional Limits Imposed by Thermodynamics during Rapid Solidification

Strict thermodynamic limits on the metastable phases that can be formed during rapid solidification could include limits on the composition range for each phase, if accurate thermodynamic extrapolations of data are available. A wide variety of measurements, phase diagrams, calorimetry, vapor pressure, EMF, etc., could serve as input data, but for most cases the data are sparse and inaccurate. The observation by C. W. White of what appears to be a upper composition limit in surface melted and regrown silicon is being examined, because in these binary systems the needed thermodynamic data seems to be available.

Relative Stability of Heterogeneous Microstructures

Work is continuing of assessing the relative stability of multiphase systems in which the individual phases may be inhomogenous and not in equilibrium with other phases present. The ranking of such structures according to their (appropiate) free energy establishes limits on what structures can evolve from a starting structure. A stability ranking of individual homogeneous phases exists only for single component systems. For multicomponent systems, metastable equilibria can be ranked, but not individual phases in multiphase systems.

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Figure Captions

Fig. 1.   The critical concentration of copper above which interface instability
occurs as a function of the interface velocity V of directional
solidification of aluminum containing copper for a temperature
gradient in the liquid of 200 K/cm. The curve is based on morphological
stability theory while the lines with negative and positive slope
correspond to the constitutional supercooling and absolute stability
criteria, respectively.

Fig. 2.   The wavelength λ at the onset of instability during directional
solidification of aluminum containing copper as a function of
interface velocity V.

Fig. 3.   Schematic representation of the predictions of eutectic solidification
theory[3].

(a)   Interface velocity vs. interface temperature. Note the maximum
in the velocity curve.

(b)   Eutectic spacing vs. interface temperature.

Fig. 4.   Thermodynamic considerations regarding eutectic solidification.

(a) α and β phases can form from liquid phase L in the shaded
area. Hence eutectic solidification is not restricted to the
"eutectic" composition.

(b)   In a complex phase diagram, many possibilities exist for
various stable and metastable eutectic reactions depending on what
phases nucleate from the liquid.

Fig. 5.   Microstructure of Pd-Cu-Si alloy directionally solidified at 0.25
mm/s. Transverse Section.

(a)   Optical micrograph. Facetted dendrites of γ phase (light) and
and interdendritic eutectic (mottled).

(b)   S.E.M. micrograph of interdendritic eutectic of γ plus a phase
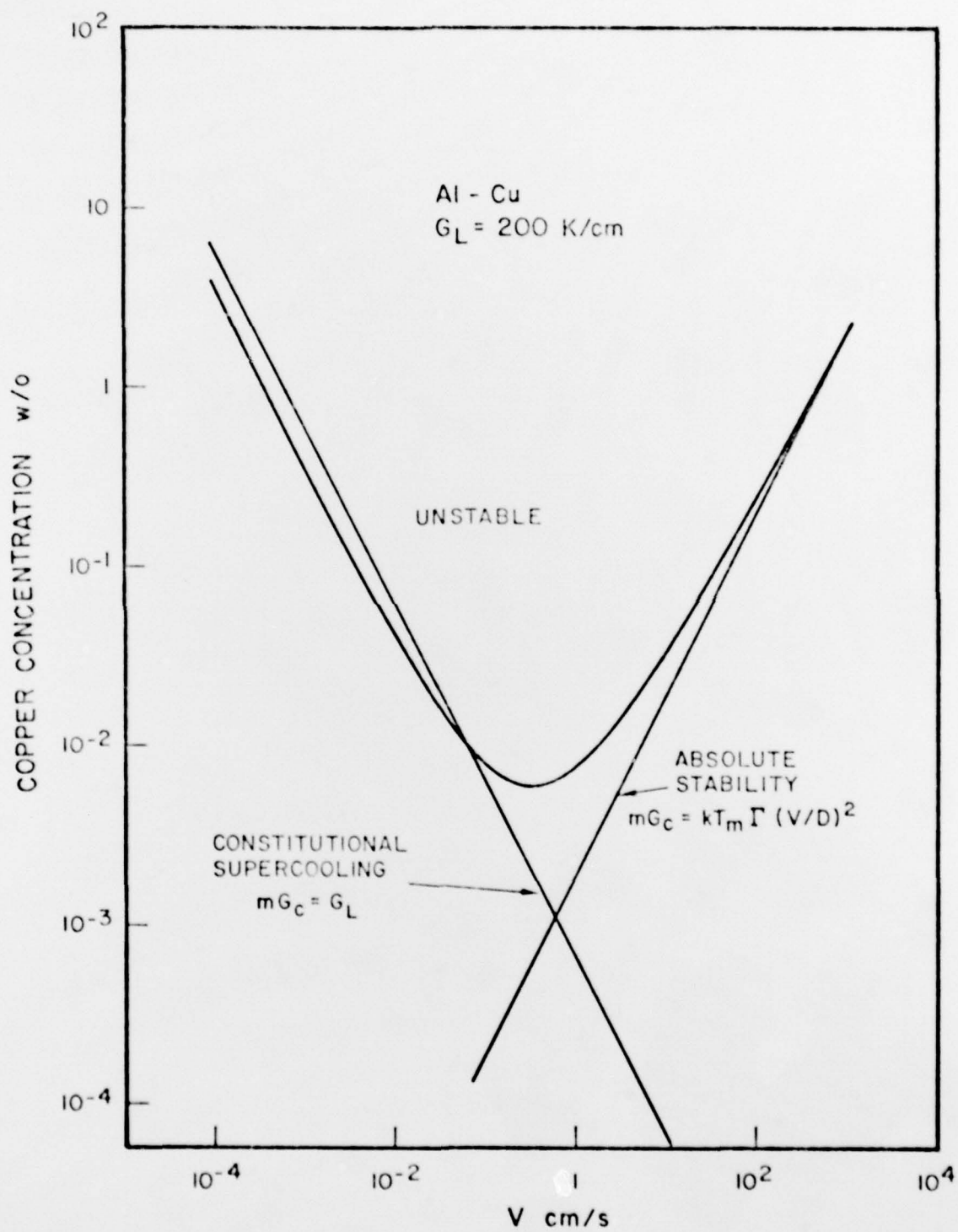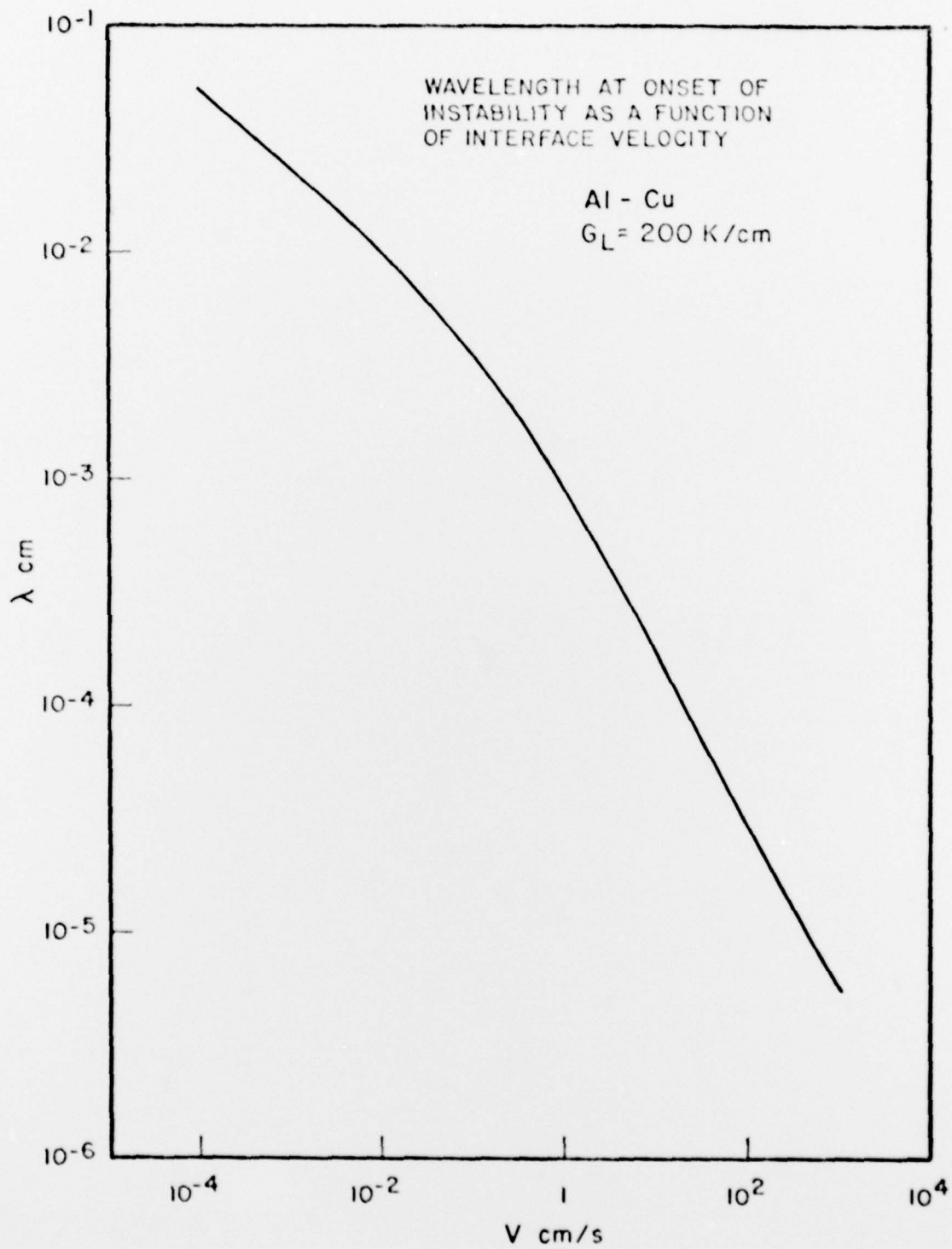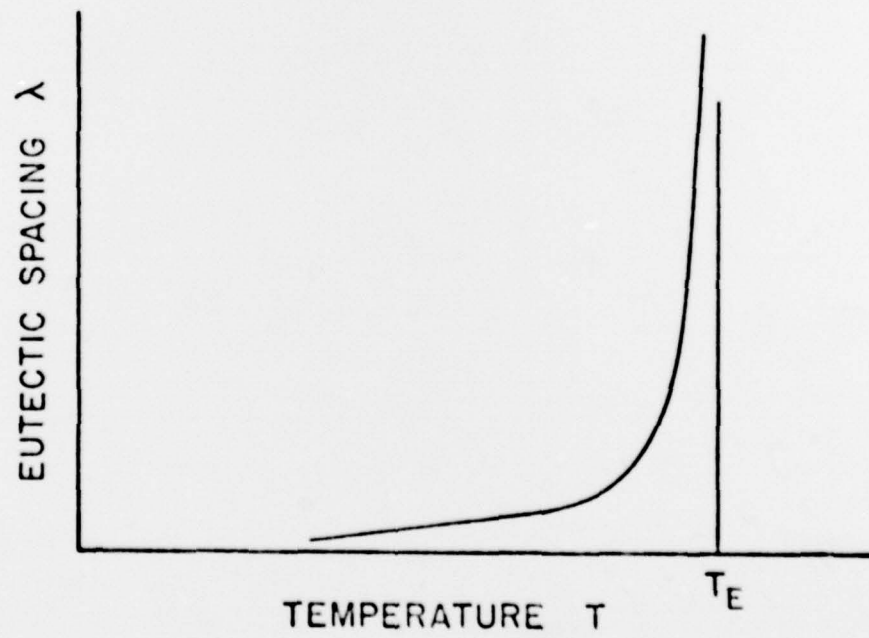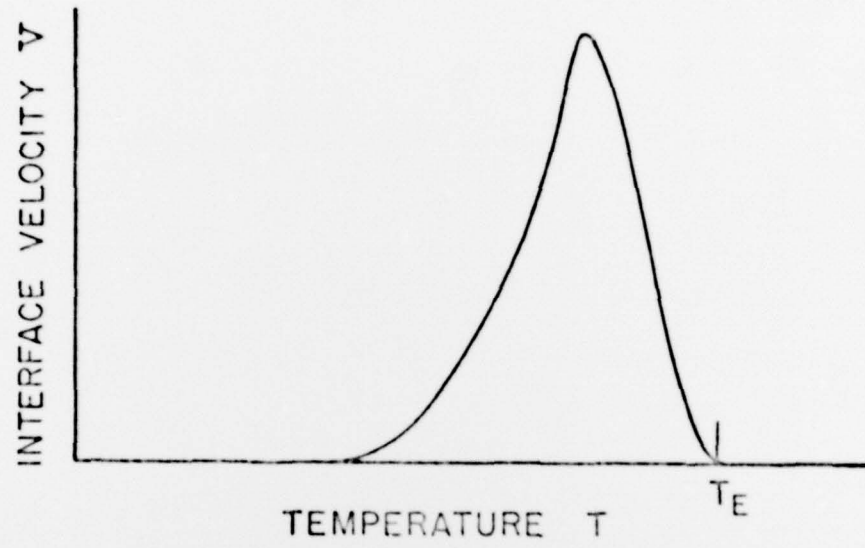κ. The γ phase is continuous with the facetted dendrites.

Figure 1.

Figure 2.

Figure 3.

(a)

(b)

(1) L → α + β   (3) L → β + δ

(2) L → β + γ   (4) L → α + γ

(5) L → α + δ

Figure 4.

(a)

(b)

Figure 5.